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LLNL-TR-652515

Prioritization Study of Elements Relevant to RIMS Counter-WMD

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March 31, 2014

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Requirement from SOW: Task 1: Prioritization study of elements relevant to countering-weapons of mass destruction (C-WMD)

A systematic study of the priority in which elements should be investigated in order to maximize the possible impact of this research. Currently, a preliminary list of the elements proposed for study, in order of interest are Pu, Am, Cm, Np, Th, and Eu. This list should be updated to reflect an order of priority based on the utility of specific isotope abundances for device diagnostics and the simplicity of developing the RIMS method for the measurement of such isotope abundances.

Deliverable – 6 months after project start, a technical report summarizing findings and conclusions of the prioritization study will be provided.

Technical Report: Task 1

Prioritization Study of Elements Relevant to RIMS Counter-WMD

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Abstract/Summary

A systematic study of the priority in which elements should be investigated in order to maximize the possible impact on RIMS Counter-WMD research has been carried out. Candidate elements included U, Th, transuranic elements, and select fission products such as Tc and Eu. This list has been updated to reflect assessments based on potential utility to debris diagnostics as well as the degree of complexity required to develop the RIMS method for the measurement of expected isotope abundances. Factors considered in this study include production of actinides in a fission environment, the existence of available resonance ionization-specific spectroscopic work, as well as practical experimental considerations (sample synthesis for research and activity/safety considerations). The resultant prioritized list of additional elements (beyond U) to be carried forward in this study are, in order of interest, Pu, Am, and Np. If resources and time lines permit, we would also like to investigate Th and Eu. Cm would be a final choice due to the logistics of creating and handling higher activity, short-lived materials, and the paucity of pre-existing spectroscopic studies.

Background and Approach

Resonance ionization mass spectrometry is a method of determining isotopic compositions in materials that excels at suppression of isobaric interferences (*e.g.*, Donohue & Young, 1983), and detection of rare and ultra trace species (*e.g.*, Wendt *et al.*, 2003). Our research has focused on the optimization of RIMS measurements in the absence of pre-analytical sample chemistry. To optimize analytical stability, an

understanding of key laser and spectroscopic parameters are required. A systematic study of the priority in which elements should be investigated in order to maximize the possible impact on RIMS Counter-WMD research has been carried out. In considering the objectives of this task, we relied on literature related to both the RIMS process and the ionization and other properties of the candidate elements, as well as discussions with debris diagnostics experts and related literature.

Excellent studies such as those by Hurst *et al.*, 1976 and Wendt *et al.*, 2005 provide a valuable summary of an element-by-element assessment of the amenability of each element to analysis by RIMS. Figure 1, excerpted from this study, provides an overview of the published RIMS spectroscopic and isotope measurement studies. Compilations of relevant spectroscopic data are available in Donohue *et al.*, 1985; Morton, 2000; Sansonetti and Martin, 2005 and others.

A RIMS Periodic Table

accessible by RIMS

published RIMS studies

published RIMS isotopic measurements

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**															
			<div style="display: flex; justify-content: space-between; padding: 0 10px;"> * LaCePrNdPmSmEuGdTbDyHoErTmYbLu </div>														
			<div style="display: flex; justify-content: space-between; padding: 0 10px;"> ** AcThPaUNpPuAmCm </div>														

Figure 1: A periodic table of elements indicating those that have been or can be explored through Resonance Ionization using presently available and under development RIMS methods. While most elements are accessible by RIMS (in red, blue and green), published studies of resonant excitation spectral levels (in blue and green) remain under development for many systems, and demonstrated isotopic measurements by RIMS (green, only) remain untapped (in great part because significant advances in laser stability have only become possible in recent years, *see* Isselhardt *et al.*, 2011).

Targeted Elements

Uranium, the most easily available and the most common element in nuclear fuel cycle materials, as well as an established component material in nuclear weapons clearly heads the list, and has already been the focus of extensive studies for precision isotopic analyses by RIMS (see Isselhardt *et al.*, 2011; Knight *et al.*, 2011; Isselhardt, 2012; Isselhardt *et al.*, *submitted*, and others). The list of additional elements beyond U that has been proposed for consideration includes Pu, Am, Cm, Np, Th, and Eu. This list reflects one rare earth element and several very heavy elements, all of which (like uranium) have significant isotope shifts (*i.e.*, differences in the exact excitation energies of the different isotopes), which require evaluated, stable laser conditions for robust application of the RIMS to isotopic ratio measurements. Using the above prioritization methodology to the list of candidate elements results in the following prioritized list of additional elements (beyond U) to be carried forward in this study, in order of interest: Pu, Am and Np (and possibly Th and Eu, if resources permit). Each of these elements is briefly discussed below. Additional discussions regarding relevance to debris diagnostics were also undertaken, but are not appropriate to the scope of the present document.

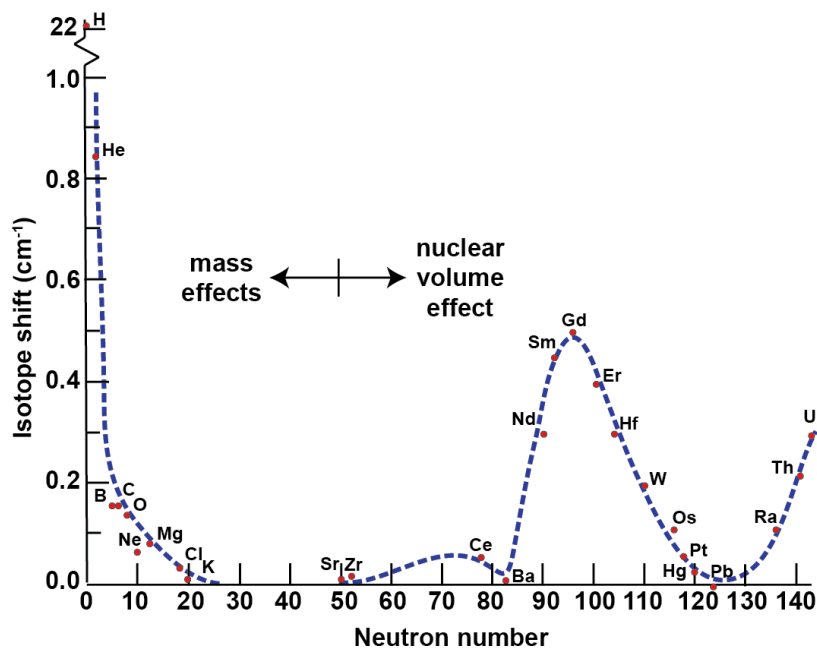


Figure 2: A diagram of average isotopic shifts by element *after* Stern and Snively, 1976. Isotopic shifts are most prominent in the lightest elements due to large mass differences between isotopes, while the heaviest elements, such as the actinides, are deformed nuclei (nuclear volume effects). Nuclear structure effects are also apparent in the rare earth element region, peaking with Gd.

Pu. Study of the plutonium system of isotopes is of obvious next importance following uranium. Plutonium is the next most common nuclear material, after uranium, used in both the nuclear fuel cycle, as well as in nuclear weapons. Plutonium concentrations in fallout are of order tens of part-per-million and lower, and suffer no dilution from environmental contributions. While the majority of RIMS studies for detection of Pu

isotope measurements work thus far has relied on combining RIMS methods with chemical pre-treatment of the sample (e.g., Donohue *et al.*, 1984; Boulyga *et al.*, 1997; Ofan *et al.*, 2006; Erdmann *et al.*, 2009), the success of measuring trace amounts of Pu by this method, including work on dissolved environmental filter samples (Eberhardt *et al.*, 1995), is well established. There is also a small body of published papers focused on optimization of Pu laser conditions and Pu spectroscopy (e.g., Sankari *et al.*, 2006; Kunz *et al.*, 2005; Kunz *et al.*, 2006). This body of existing work, including key spectroscopic studies, enables rapid transfer of our RIMS modeling methods to the Pu system. Pu-bearing samples are readily available in a variety of forms, such that minor additional parameters required for modeling and study efforts can be established.

Am and Np. Both americium and neptunium are transuranic elements formed primarily through nuclear reactions on and/or decaying to uranium and plutonium. Thus, in any nuclear event involving uranium or plutonium (from reactors to weapons), isotopes of both Am ($z=95$) and Np ($z=93$) would be expected to be generated, and can lend complementary understanding to fuel isotope measurements. For americium, several isotopes can be created which have significant half-lives and production probabilities. ^{241}Am , produced from decay of ^{241}Pu , is the most common, and has a 432 year half-life. ^{243}Am is longer lived (7370 years), and can be also produced through neutron irradiation of plutonium, as is well established through spent fuel studies. Likewise, two longer-lived isotopes of neptunium are produced through neutron irradiation of uranium or plutonium (^{237}Np with a half life of 2.14 million years, and ^{239}Np , which decays to ^{239}Pu with a 2.4 day half life). Preliminary studies of the excitation and ionization schemes of both Np (see Reigel *et al.*, 1993; Raeder *et al.*, 2011) and Am (see Deußenberger *et al.*, 1995; Kohler *et al.*, 1997; Fivet *et al.*, 2007) have been published, including, for example, a report of RIMS detection of $^{242\text{m}}\text{Am}$ fission isomers (Backe *et al.*, 1992), but some research is still needed to obtain key measurements of hyperfine structure and transition probabilities.

Th. Although not a trans-uranic element, thorium ($Z=90$) is also of interest to nuclear materials measurements. All thorium exists in nature as ^{232}Th , and is seen in geologic materials in generally in part-per-million concentrations. Additional isotopes of Th, however, can be produced through the uranium decay chains. In particular, ^{230}Th is the product of ^{238}U and ^{231}Th is the product of ^{235}U decay. An array of thorium isotopes is thus expected in a uranium system in the presence of neutrons, and can be used to characterize a system exposed to a high-neutron environment. Focus on the potential of the $^{230}\text{Th}/^{232}\text{Th}$ geochronometer has advanced resonance ionization work in this area (e.g., Johnson *et al.*, 1992; Billen *et al.*, 1993; Raeder *et al.*, 2011).

Eu. In addition to consideration of the above heavy elements, we also considered RIMS analyses of fission products. The isotopes of Europium are potential candidates as europium ($z=63$) isotopes (such as ^{155}Eu) can be created through nuclear fission, and can also be produced as a neutron activation product (e.g., ^{152}Eu and ^{154}Eu) from naturally occurring environmental materials. Eu is one of the few fission products where there are significant long-lived isotopes unique to the event representing both a high yield fission product and a common activation product. That said, Eu isotopes are present in part-per-

billion concentrations in post-detonation debris amid part-per-million concentrations of environmental isotopes. Such low concentrations are unlikely to be measurable by RIMS though direct application of the present analytical methods using no chemical pre-concentration with the presence of significant environmental backgrounds. Recent studies suggest, however, that fission products may have heterogeneous spatial distributions in such materials, affording RIMS (inherently a spatially resolved technique) a niche through the targeting of highly concentrated areas of interest within single pieces of fallout glass. Recent spectroscopy data are available (Nakhate *et al.*, 2000), and Eu isotope measurements by RIMS have been reported in environmental wastewater (Khalmanov *et al.*, 2002).

Tc. Technetium ($z=43$) is one of the few non-naturally occurring elements (the other being promethium, $z=61$) with $z < 84$ (Po). It has no stable isotopes. Studies for RIMS have focused on detection of the daughter product Ru (Savina *et al.*, 2004), and spectroscopic measurements of ionization potentials (Kluge *et al.*, 1994; Passler *et al.*, 1997). Tc is of interest as a near-zero background fission product. Because it contains no stable isotopes and has significant activity, however, it must be produced for measurement and handled with considerable care, make it non-ideal for current studies though of future interest.

Cm ($z=96$), Bk ($z=97$), Cf ($z=98$), Es ($z=99$), Fm ($z=100$). These transuranic elements can all be of interest, as they may be produced in trace or ultra-trace amounts from neutron reactions on plutonium and other transuranic elements in high yield (mega-ton) nuclear events (Fields *et al.*, 1956), and have near-zero natural backgrounds. Fermium on the order picograms of was reported in kilograms of debris recovered from the 1969 'Hutch' event (Hoff and Hulet, 1970). Cm, Bk and Cf can occur as isotopes with half-lives on the order of years, while no isotopes of Es and Fm have half-lives longer lived than hours to days, and are not naturally present even in trace amounts. Studies with these elements are accordingly limited by isotope production, and have generally been undertaken in collaboration with beam line or other production facilities. Determinations of the first ionization potentials for these elements by RIMS are published (*e.g.*, Erdmann *et al.*, 1998; Peterson *et al.*, 1998; Sewtz, *et al.*, 2003), demonstrating these elements can be resonantly ionized. Due to limited sample availability and research logistics, however, other significant RIMS research remains scarce, and would require non-trivial investment.

Conclusions

The results of this study confirm the priority preferences anticipated for the first two years of the overall NPS-RIMS project, with Pu being the focus of the first year and Am and Np being added to the study for year 2. The prioritization study, in addition, provides some additional insight into follow-on emphasis in terms of potential additional elements to be added in future efforts.

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-TR-xxxxxx.